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RESEARCH AND DEVELOPMENT IN THE GLASS FIBER
SODIUM-SULFUR BATTERY

Charles A. Levine

Dow Chemical U. S. A.

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SODIUM-SULFUR BATTERY

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Charles A. Levine
Principal Investigator
Phone: 415-933-3100

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SUMMARY

I. Technical Problem

The hollow fiber sodium-sulfur cell has been shown to have outstanding electrochemical characteristics. The major problem now is to obtain increased lifetimes and still maintain the good performance. We must demonstrate projected lifetimes of "years" and thousands of cycles in cells which do not change characteristics with total time in operation.

II. General Methodology

By observing the mode of failure of operating cells we have been able to separate those factors that cause shortened lifetime into several categories.

They include: (1) glass fiber weakening at the tube sheet due to reaction with the tube sheet material; (2) mechanical configurations or damage that puts excess strain on parts of the cell; and, (3) degradation of the fiber itself as a function of its electrochemical environment.

The causes of fiber weakening at the tube sheet have been defined and, for the most part, solved. Causes due to mechanical factors, such as bad seals on the fibers, have in part been found and are being corrected. Degradation of the glass fiber itself is being attacked in another manner.

Small assemblies have been built in which degradation from the sodium side can be isolated from degradation occurring on the sulfide side of the cell. These assemblies allow us to run Na-Na cells in which we can change the quality of the sodium anolyte, the current density, and the number of column volumes of sodium charged or discharged per cycle. Since there is no sulfur-sulfide or metallic cathode pickup foil in the assembly, only the interaction of the glass and the sodium (with its impurities) is studied.

Once the sodium anode is understood and stabilized for long-term operation, similar assemblies will be used to study the effects of the catholyte side of the cell; sulfur quality, cathode material, and the alloys to be used for the case.

Correlations of cell life versus current density are being made to try to find a valid method of accelerated testing of cells.

As information from the small testing assemblies becomes available, the process changes which are suggested are incorporated into five ampere-hour and larger cells. The increased lifetimes of these cells give practical confirmations that the degradation processes involved are indeed lifetime limiting phenomena.

III. Technical Results

During this period, lifetimes of operating cells have increased substantially. Cells with 1000 fibers (0.3-0.4 ampere-hours) have operated on continuous charge/discharge for over 3200 hours (1640 cycles) at 25% depth of discharge. Larger cells, 5 ampere-hour, have been charge/discharged cycled up to 80 days at 10-25% depth of discharge, and 18 days at over 80% depth of discharge. Prior to this reporting period, lifetime for the five ampere-hour cell was limited to 23 days. Cell resistance changed only a few percent during the life of the cell.

The major factor in increasing cell life was the strengthening of the fibers at their junction with the tube sheet. This was done by removing the water in and on the tube sheet glass powder before it is fused into a tube sheet. Since we began to remove the water from the tube sheet powder before fusion, no cell failures due to fiber failure at the tube sheet have been observed. Another factor in increasing cell life was increasing the quality of the glass fibers, especially in regard to the end seals of the fibers and fiber cross-overs during the spinning and assembly processes.

We have found, from Na-Na cells, that the calcium impurity in the sodium causes "blocking" of the sodium electrode during discharge, increase in resistance, and early fiber breakage. We do not yet have lifetime

data from large Na/S cells showing the effect of using calcium-free sodium. However, on small cell assemblies run at very high current densities, calcium containing sodium causes fibers to break in hours, while "clean" sodium results in lifetimes of "weeks".

Very early stage experiments suggest some degradation of the fiber by some component in the catholyte chamber also. We are just beginning to work on this.

A mock-up of a 50 ampere-hour cell (6.6 amperes, 8 hours) was made on existing equipment with no problems.

Five ampere-hour cells designed for 16 hour cycles were made and run without difficulty. Internal cell spacings are larger to accommodate the required catholyte.

Fiber spinning has been improved with the upgrading of cutting and sealing the fibers and of fiber assembly. Overlapping of fibers with the subsequent scratching and weakening has been decreased by getting straight lay-down tapes.

After discovering the disastrous effect of water in the tube sheet, techniques have been mostly worked out for making DRY tube sheet powders from the tube sheet glass. Most of the grinding and sieving is done in a dry box.

Quality control points have been defined for the assembly of the cell and standards are being set.

IV. Implications for Further Research

Goals are still to increase cell lifetime and to determine a method of running accelerated lifetime tests. Now that the cells seem structurally adequate, we are determining the effect of impurities in the sodium chamber and in the sulfide chamber. Calcium in the sodium chamber seems detrimental. We will determine if the other major impurity, potassium, is detrimental.

In the sulfide chamber, there are organic residues, aluminum, magnesium, carbon, and all of their impurities.

We will isolate each of these and see the effect on the glass at normal and at very high current densities.

We hope the very high current densities will act as an accelerated life test. This is being determined.

Further drying of the tube sheet glass should result in even stronger fibers at the tube sheet-fiber juncture.

Upgrading of the fiber and cell assembly processes will be done so these processes can be turned over to non-professional workers.

Larger cells will be constructed and run as "proof-of-scale-up".

Quality control procedures and standards must be developed to give good base-line operation of the cells.

INTRODUCTION

This is a report on the Development of the Hollow Fiber Sodium-Sulfur Battery covering the period January 1, 1975, to June 30, 1975. Much effort has gone into finding the causes of cell failure and determining how to remove or mitigate these causes.

The hollow fiber sodium-sulfur cell has been shown to be capable of reproducible voltage characteristics over several thousand charge/discharge cycles at high efficiencies. It is potentially an inexpensive, light weight energy storage device. The target for the development effort during the period has been to improve the lifetime.

Cell failure has been ascribed to fiber breakage during cell operation. Many times the fiber breaking occurred immediately below the tube sheet. Other times fibers broke in the working body of the fiber. It was apparent that the fibers were weakened substantially in the vicinity of the tube sheet during the processes of cell assembly. Part of the program was to determine why this happened and correct the situation.

Other parts of the program include improving on the methods of making the components of the cell and testing and evaluating working cells under various regimes of charge and discharge.

Cell lifetime at the beginning of this period was about 2 months for the 1000 fiber cell and 20 days for the 5 ampere-hour cell operating at 10-25% depth. At >80% depth of discharge, the 5 ampere-hour cell lasted about one week. These lifetimes have been substantially improved.

RESULTS

Task I - Back-up for Fabrication Operations

Fiber Glass Spinning. Substantial improvements have been made in the spinning, take-up, and assembly of the hollow glass fibers. Modifications were made on the jet cooler that cools the molten glass as it emerges from the spinnerette. Circular tangential jets were tried and discarded. The present cooler is an array of 10 cooling nozzles placed 5 on each side of the glass stream. A well centered hole results. With this cooler, fiber dimensions are held to $\pm 5\%$ over a fiber size range of 40 x 90 μ to 50 x 70 μ . The cooling limitation holds maximum fiber size to 40 x 90 μ for good quality fibers and also sets the maximum spinning feed rate.

Automatic cutting and sealing of the fibers has been upgraded. At the first of this period, the cutting and sealing were not reproducible. The end sealing of the fibers was poor and some cell failures could be attributed to "hook-like" or "drawn out" ends on the fibers. A preliminary effort showed that a laser could be used to cut and seal the fibers instead of hot nitrogen, but, in both cases, focus is extremely important. Microscopes were mounted on the spinning apparatus so that the quality of the end seals could be monitored during a spinning run. An attempt was made to hold the fibers in place, i.e., in focus, during the cutting and sealing by the hot gas by means of a presser foot. Unfortunately, the presser foot gets gunked up with glue from the tape. Hot helium was tried as a cutting gas, but was discontinued because the flow rates were very critical.

The 0.5 mil aluminum tape that is used to hold the fibers in correct juxtaposition relative to each other has been a source of problems. When the tape does not feed in a straight line, it bends the fibers and causes overlapping of the fibers with subsequent scratching and weakening. A number of changes were made to lessen the "wandering" of the tapes. Better tape guides were designed and installed. The presser wheels which press the glue-containing tapes onto the fibers were changed from teflon to a soft silastic and moved to within 1/2"

of the fiber lay-down paint. The applicators which put the glue on the tape were redesigned to prevent the glue from going over the edge of the tape and causing gross sticky areas.

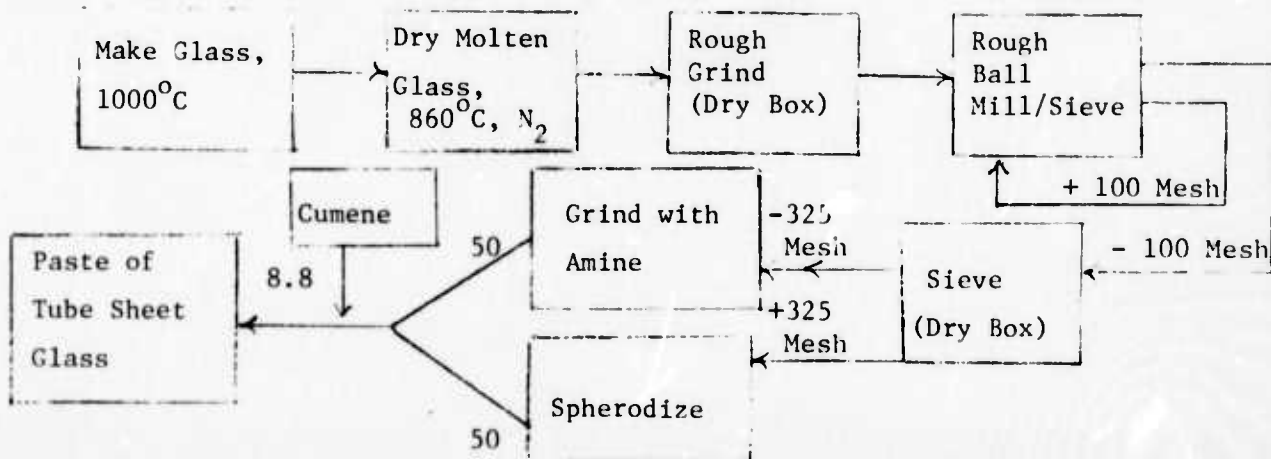
Foil Coater. A few changes were made to the foil coating machine to improve its operation. The Aquadag feed is now done continuously with a syringe pump rather than having it a hand operation. New applicator blades of rather soft rubber are being used. These changes have allowed coating speed to be increased from 18"/minute to 46" per minute.

Manufacture of Tube Sheet Material. The tube sheet material made from 95.5% B_2O_3 -4.5% Na_2O continues to give longer cell lifetimes than the 94% B_2O_3 -6% Na_2O . It matches the fiber glass expansion coefficient better and it is fused at a lower temperature. A batch of 96% B_2O_3 -4% Na_2O was made and tested. It matches the fiber glass expansion almost exactly and fuses at a still lower temperature.

Glass	Exp. Coeff.	Temp.	Fusion Temp.
406 fiber glass	121 (10^{-7})	500°C	-
94/6	110 (10^{-7})	400°C	385°C
95.5/4.5	116 (10^{-7})	363°C	374°C
96/4	122 (10^{-7})	-	366°C

It should ultimately be better than 95.5/4.5, but the sample made did not mix up into an extrudable paste.

We have known that high water contents in the tube sheet glass weaken the glass fibers. Apparently during the fusion of the tube sheet, the water attacks the fiber glass. We developed a technique of analyzing the glass for water content and found the tube sheet glass picked up a great deal of moisture during its preparation. A flow sheet of the tube sheet glass preparation is shown:



After drying, the tube sheet glass has 0.0033% H_2O . After the rough grind, the water content is 0.03%. After the rough ball milling, the water content is 0.06%; and after sieving the water content is 0.3%. The sieving could not be done properly in the dry box because of the highly charged nature of the fine glass particles. We are now attempting to dissipate the charge by the use of X-rays. As will be mentioned later, we have circumvented the effects of the water in the tube sheet glass by reacting it with BCl_3 before the tube sheet is fused.

If the tube sheet glass powder is left in dry laboratory air for one hour, the water content goes from 0.3% to 0.34%; for 5 hours, to 2.5%.

Grinding the fine powder with amine goes on for 7-10 days. The glass powder picks up a lot of water at this stage even though pains were taken to seal the ball mill against outside air. We now do this grinding in a dry box to minimize water pick-up. Unsuccessful attempts were made to dry the powder after the amine grinding (removing the amine in the process) and then re-add the amine surface active agent.

The fiber glass also is wet. It normally has a water content of about 0.04%. Bubbling N_2 for one hour through an open dish of the melt at $1000^{\circ}C$ only drops the water content to 0.03%.

Quality Control on Glasses. During most of this period, the analytical determination of elements in the glass was very unsatisfactory. We now get pretty fair results for sodium and chlorine, and mediocre results for silicon. The scatter of the results are:

$$Na(\text{theo} = 22.4\%) = 22.0 \pm .3\%$$

$$Cl(\text{theo} = 2.55\%) = 2.55 \pm .05\%$$

$$Si(\text{theo} = 2.52\%) = 2.5 \pm .15\%$$

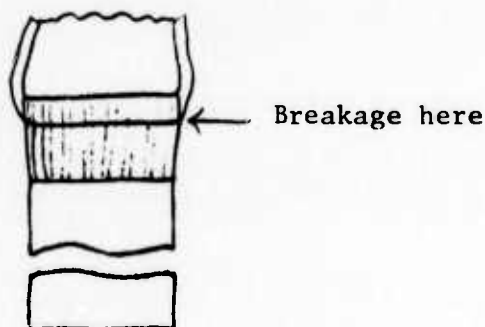
The strength of the glass fiber was determined at each step in its manufacture and assembly into a cell. The tensile test was a pull test on a 4-inch long piece of fiber.

<u>Glass</u>	<u>Tensile, psi</u>
Freshly drawn (before pulleys)	132,000-98,000
New fiber, exposed 1-10 min., then 1 hr. @ 300°C vacuum	73,000-40,000
New fiber, laboratory air, 3 days	81,000-78,000
Fibers from assembled cell	~48,000
Fibers from fiber storage before cell assembly	49,000-42,000

It appears that heating the glass fibers either sensitizes them or removes surface tensions so the resultant fiber appears weaker. Weakening during fiber storage may be a function of how well they are sealed during storage. Some preliminary data indicate that with proper storage, they do not weaken so badly.

Task II - Improvement on Fiber Weakening at Tube Sheet

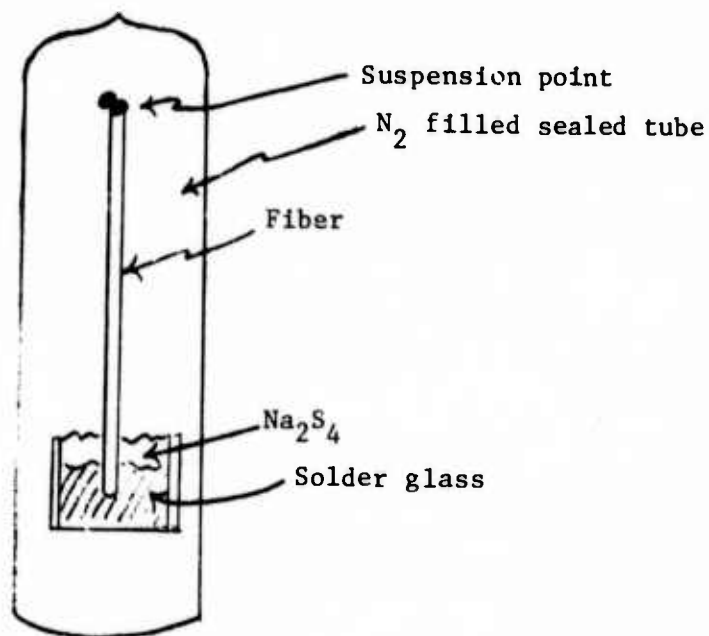
At the beginning of this reporting period, most all failures occurred with the fibers breaking at their junction with the tube sheet.



The tube sheet glass was changed from 96/4:B₂O₃/Na₂O to 95.5/4.5:B₂O₃/Na₂O to improve the expansion coefficient match but failures directly under the tube sheet were still being experienced.

Tests were designed to determine whether the junction of the tube sheet glass and the fiber glass had an enhanced susceptibility to corrosion by Na₂S₄. A small holder was potted on the end of a glass fiber using the tube sheet glass as the potting material. The holder was filled with Na₂S₄ and the fiber suspended so the fiber was under tension at the

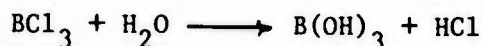
junction. These assemblies, in N_2 , were held at $300^{\circ}C$ for over one month. No breaks occurred on the fibers.



Other samples of the glasses were held for 2 weeks in Na_2S_4 at $300^{\circ}C$ and the surfaces examined by electron microscopy for roughness. No roughness was seen. We concluded that in static tests, the Na_2S_4 does not corrode the fiber or the tube sheet or their juncture.

When we were able to determine that the tube sheet glass did indeed have a much higher water content than we had thought, we postulated that the water in the tube sheet glass was attacking the fibers. It would be especially bad during the fusion of the tube sheet since the mobility in the glass is very high. We are now developing procedures for keeping the tube sheet glass dry during its manufacture.

Another approach was to dry the glass powder before it is fused into a monolithic tube sheet. After the bundle is made, but before the tube sheet is fused, the whole bundle is treated with BCl_3 gas at about $150^{\circ}C$. The BCl_3 reacts with the surface water in the non-fused tube sheet powder compact,



Vacuum is applied to remove the HCl and the tube sheet is then fused. The remaining boric acid simply adds a small amount to the 95.5% B_2O_3 tube sheet material.

Since we have begun using this treatment, we have only very rarely experienced any fiber failures at the fiber-tube sheet interface.

Task III - Cell Testing and Evaluation

Lifetimes of operating cells have increased substantially. Graph I shows the improvement with time. Small 1000 fiber cells have operated for more than 4 months or 3290 hours on constant 4 hour charge/discharge cycles before failure. The longest lived of these cells had 1640 cycles at 25% depth of discharge. The 5 ampere-hour cell has operated for over 80 days on similar charge-discharge cycles at 10-25% depth with invariant output characteristics before failure. However, when the 5 ampere-hour cells are discharged to over 80% of capacity, lifetime has been limited to about 18 days. The deep cycling is done at 8 to 20 hour rates.

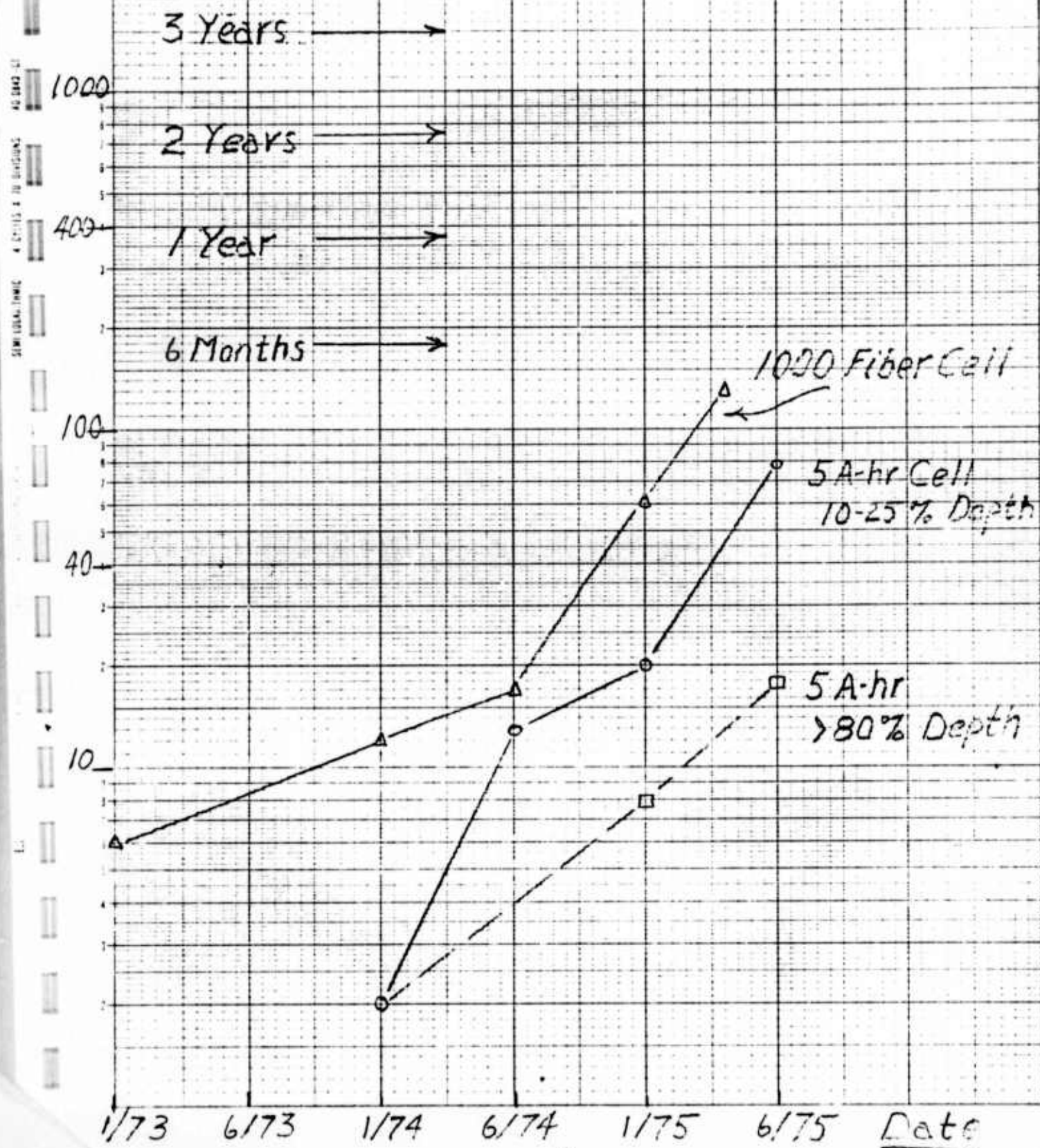
One of the major factors of the increase in lifetimes is the strengthening of the fibers at the tube sheet, as described above. Cell failures are now almost totally due to fiber failures in the body of the cell.

The longer lives have been attained with glass fibers having 20-25 μ wall thicknesses. Glass fibers with this wall thickness are feasible for even one hour rate cells. We have, therefore, stopped using 10 μ wall fibers except in experimental assemblies as described in the next section. The only disadvantage of using the thicker fibers is that more glass (weight, cost) is used in the battery.

Cells now being built and run incorporate the latest improvements. The cells are being filled with "calcium-free" sodium and the cathode foils used are thoroughly baked out to remove organic impurities. Based on the results described below, these should have very long lifetimes.

A mock-up of a 50 ampere-hour cell (6.6 amperes, 8 hour) was rolled using the existing equipment. This cell had 12000 fibers, 50 x 90 μ , spaced 33 per cm. There were no problems in the rolling or assembly of this size cell.

Graph I Lifetime of Multifiber Cells



For use as power storage rather than motive transport, a capacity larger than one hour is desirable. Many cells have been built and run that have 6-8 hour capacities and more. Foil-foil spacing is increased from 100 μ to 125 μ , and fiber-fiber spacing is increased from 100 μ to 300 μ . There were no problems in assembling these cells or in their operation.

A test rack for running 12 five ampere-hour cells was designed and built. The cells can be charge/discharge cycled at up to 5 amperes on timed cycles or can be cycled with voltage switching. They can be individually continuously discharged or left on open circuit. Voltage versus time plots are maintained on each cell. Charge or discharge currents are set for each cell by load resistors.

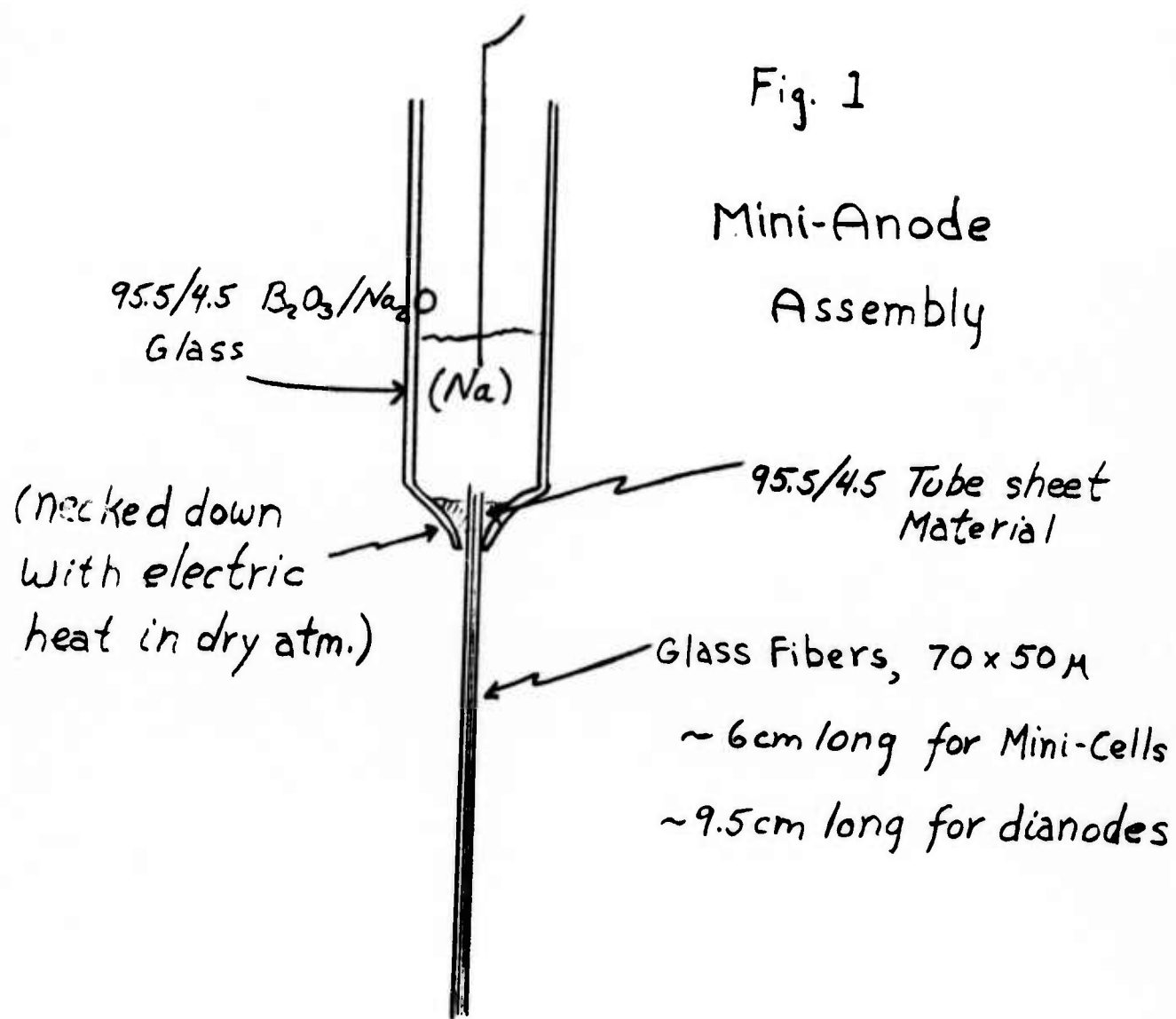
Another test rack was designed for handling up to 25 forty ampere-hour cells. A one cell prototype is being built.

Task IV - Mechanisms of Cell Degradation

With the enhanced strength of the fibers at the tube sheet, cell failures occur in the body of the fibers. In order to rule out failures due to poorly sealed fiber ends, the ends of all fibers put into the cells are inspected. If poor seals are found, the fibers are discarded.

A tool for finding the causes of cell failure is a mini-anode. It consists of only 6-8 fibers potted into a holder made of the tube sheet glass. It is shown in Figure 1. With this assembly breakage of a single fiber can be readily detected by the change in electrical resistance. This mini-anode introduces no impurities into the system by itself. Various "qualities" of sodium, sulfur, and aluminum can be used with it to determine the effect of impurities on fiber life. Some postulated causes of glass fiber failure have been impurities in the sodium, impurities in the sulfur, and alloying agents in the aluminum cathode pick-up foil.

Preliminary results using these mini-anodes immersed in Na_2S_4 indicated that high current densities gave shorter fiber lifetimes. Later data showed that the high current density per se did not cause shorter lifetimes, but deep cycling did. Some cells, run at three times design current but only about 10% depth gave lifetimes of up to 59 days (1400 hours) and 4200 cycles.



These cells, in general, showed a small increase in cell resistance during the first 5-10 days and then held a more or less constant resistance. There was a slight indication that cell resistance increased a few days before failure. There seemed to be no difference in cell performance over a period of about a month whether the cathode pick-up material was stainless steel, molybdenum foil, carbon on aluminum alloy 5005, or molybdenum on the aluminum alloy 5005.

In order to get a better measure of whether a resistance increase was occurring, a more sensitive voltameter was obtained. Accurate resistance measurements can now be obtained at about 0.5% accuracy instead of 4% accuracy. A reference electrode was built into the mini-cell. The reference electrode was a fine closed end tube made out of the fiber glass and into which a fine aluminum wire was threaded. Once the cell was assembled, the reference electrode was partially filled by charging it with Na from the Na_2S_4 .

Using the more accurate measurements, it was determined that the cell resistance usually increased a few percent before cell failure. The reference electrode measurements showed that the increase was associated with the glass fiber or the glass fiber surface rather than with the sulfide or the cathode pick-up. The rate of resistance increase did depend on the current density.

In order to isolate the source of this effect, i.e., whether it was related to the sodium/glass or the glass/sulfide, "dianode assemblies" were built (Figure 2). With these assemblies, one sodium anode charges while the other discharges. By putting a reference electrode in the sulfide pool, one can determine whether the resistance build-up is due to a charging mechanism or a discharging mechanism.

The results showed a resistance build-up on the discharge electrode, where sodium is going from the inside of the fiber, through the glass, into the sulfide pool. Graph II shows some typical results. After one column volume of sodium is discharged, the glass resistance increases. The sodium is a filtered, reagent grade. It contains .04% calcium and 0.01% potassium as the major impurities.

Whenever there was a prolonged resistance increase due to a continued discharge, a fiber failure occurred within several hours.

When sodium that was free of calcium was used, no resistance build-up occurred. Graph III shows typical results. In all of these experiments, current density was about three times the design rate. Calcium was removed from the sodium by heating the sodium for 1 1/2 hours at 300°C in the presence of Na_2O . The metal was then cooled to 125°C and filtered through a medium frit. The Ca content dropped from 0.04% to 0.0015%.

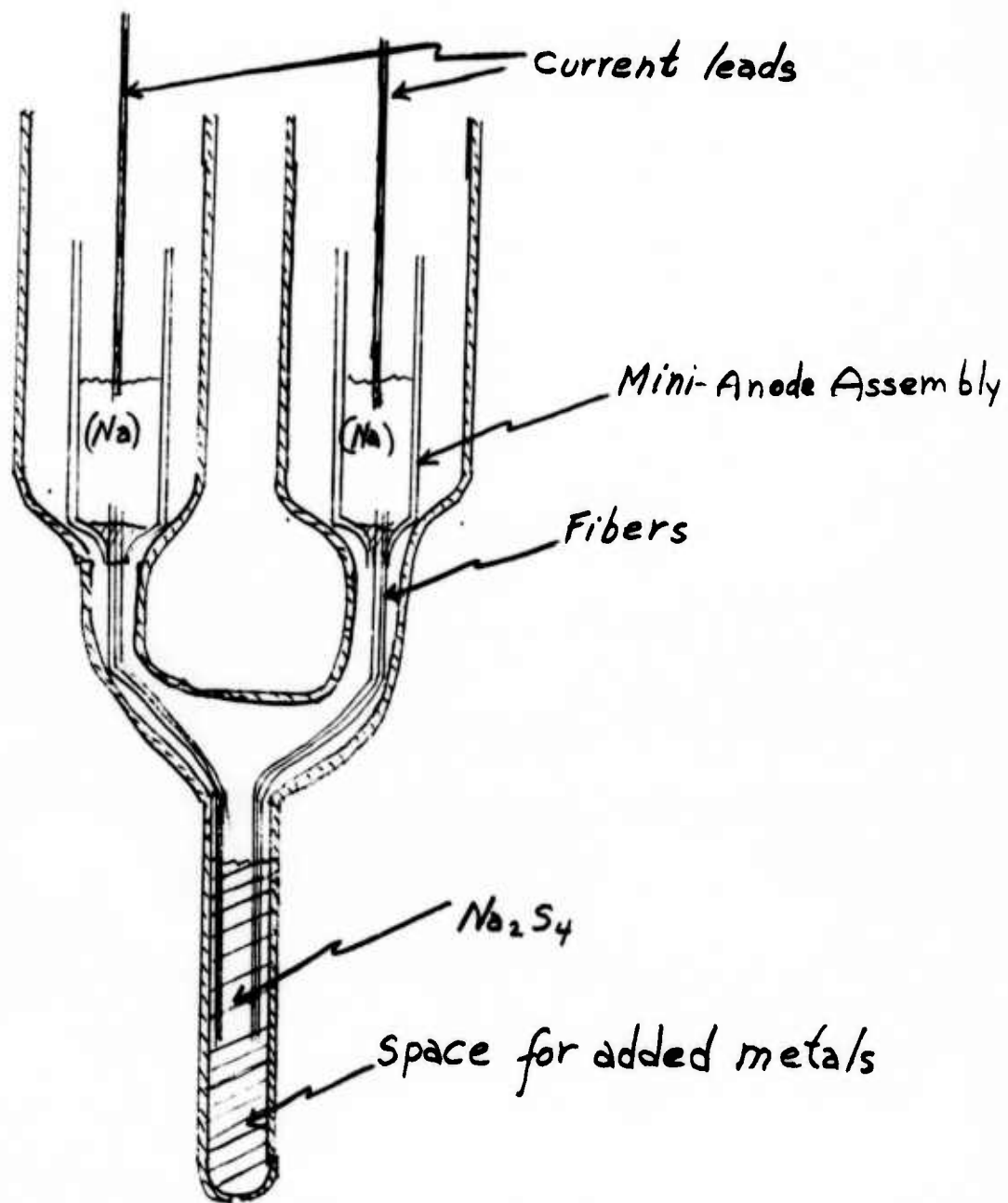
Lifetimes of the fibers are very much longer using Ca-free sodium in the dianode assemblies than when the normal sodium is used. Lifetimes are "weeks" instead of "days" under the conditions of operation. Eventual breakage of the fibers using "clean" sodium is at the point of bending and strain in the assembly---above the sulfide pool.

The initial drop in anode resistance seen in Graph IV is puzzling. It may be due to a slow sodium wetting of the fiber or to wicking of the sulfide up the outside of the fibers.

Similar cells are now being constructed in which sodium is placed both inside and outside of the fibers. This should pin down the role of calcium in the sodium. We are trying to get some sodium that is also free of potassium to make comparisons.

With calcium-free sodium, we should get reproducible anode assemblies which behave in a non-variant manner. We will then begin to look at the effect of various parts of the cathode and catholyte system. The first experiments using the mini-anode assembly seem to confirm that with some metallic cathodes, glass resistance rises during the charge part of the cycle. We are trying to define the specific metal or impurities responsible.

CAL:jd
7/28/75



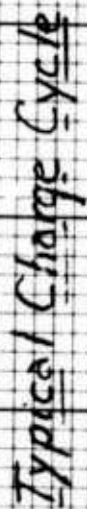
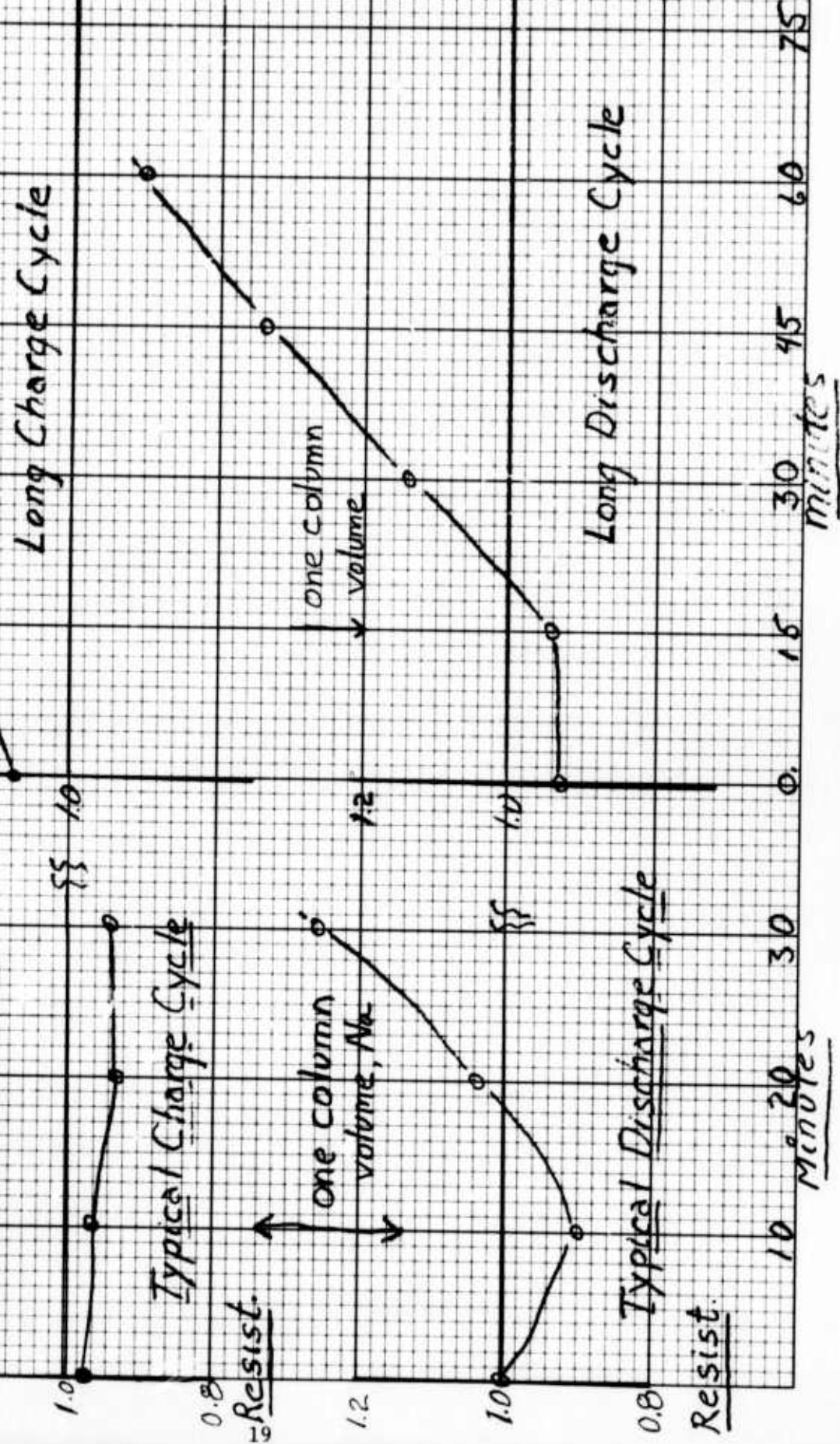
Di Anode Assembly

Fig. 2

Graph 11

Resistance

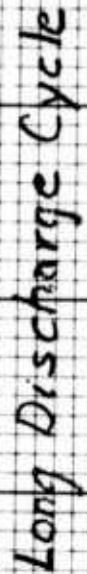
Diode Assemblies -
filtered No. (0.93(a))



Resist.

one column
volume Na

one column
volume



Typical Discharge Cycle

Resist.

10 minutes

30	45	60	75
minutes			

